(54) **Amorphous polyolefins**

(57) Amorphous polyolefins include units derived from a mono-olefin such as ethylene and/or propylene and units derived from a norborene type olefin of the formula (I):
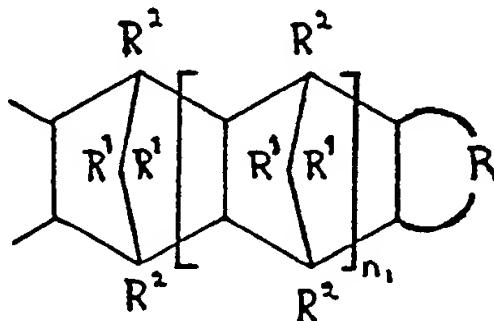
(I)

where $-n_1$ is 0,1 or 2; R is a divalent aromatic group; or together with the carbon atoms (of the norbornene ring) to which it is attached forms an aromatic group; and each R^1, and each R^2 is independently a hydrogen, halogen, alkyl or aryl. The polymers can include units of other norbornene type monomers. The polymers are amorphous, typically being clear and uncoloured and have high T_g values and can be used in optical components, e.g. optical discs, CD-ROM or optical fibres.

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1990.

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AMORPHOUS POLYOLEFINS

This invention relates to amorphous polyolefins and in particular to amorphous copolymers of low molecular weight acyclic, particularly alpha-aliphatic olefins such as ethylene and/or propylene with bridged ring olefinic monomers especially norbornene derivatives.

Polyethylene and (isotactic) polypropylene are crystalline polymers having good chemical, particularly solvent, resistance and are substantially unaffected by moisture. They have relatively low glass transition temperatures (T_g) and thus have low strength at elevated temperatures. Being crystalline, they are translucent rather than optically clear in the wavelength range of visible light. Their low strength and relatively poor optical properties mean that these polymers are not suitable for applications such as optical disks, optical fibres and other similar optical components. It has long been known that higher T_g amorphous polymers can be made by copolymerising ethylene with norbornene and certain derivatives, for example as described in British Patent Specification Nos. 777414, 951022, US Patent Specifications Nos. 2799668 and 2883372, West German Offenlegungsschrift No 2421838 and East German Patent Specifications Nos. 215087, 222317 and 246903.

More recently a number of specifications in the name of Mitsui Petrochemical Industries have been published, including European Published patent applications Nos. 0156464 A (US equivalent No 4614778), 0203799 A, 0291208 A, and 0310394 A, which develop the idea of making amorphous polyolefins copolymers based on ethylene or a similar aliphatic monomer and derivatives of norbornene such as 6-methyl-1,4,5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene (MDMON).

The present invention is based on the finding that certain cyclic aromatic substituted derivatives of bridged cyclic olefinic monomers can give clear amorphous copolymers with acyclic olefins having a good combination of optical, mechanical and physico-chemical properties. This combination of properties makes these copolymers candidates for use in optical products such as optical discs, especially CD-ROM, WORM and erasable or re-writable optical discs, optical fibres and related devices and components.

Accordingly, the present invention provides an amorphous polymer containing units derived from an acyclic mono-olefin and units derived from a

norbornene type olefin including units of the formula (I):

(I)
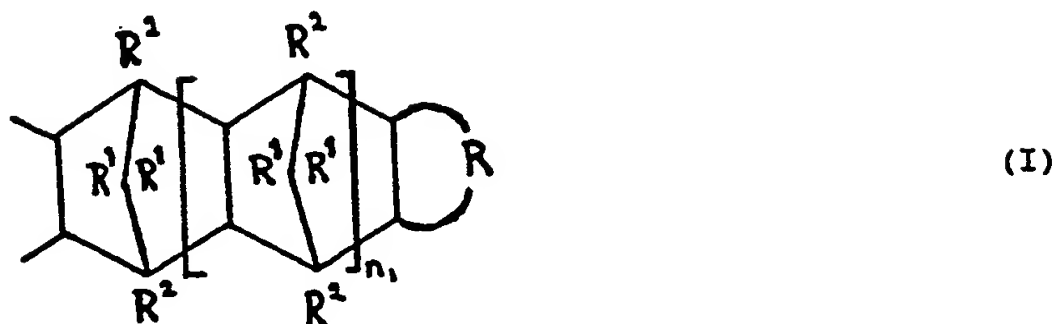
where:

n₁ is 0,1 or 2;

R is a divalent aromatic group, particularly a 1,2-phenyl or a
1,8-naphthyl group; or together with the carbon atoms (of the norbornene
ring) to which it is attached forms an aromatic group particularly a
1,2-phenyl group (especially when R is a :CH.CH:CH.CH: group); and

each R¹, and each R² is independently a hydrogen or halogen atom or an
alkyl, particularly a C₁ to C₄ alkyl, group or an aryl, particularly a
phenyl, group.

The invention includes a method of making an amorphous copolymer as
defined above which comprises, polymerising a mixture of at least one acyclic
mono-olefin and at least one monomer of the formula (II):

(II)
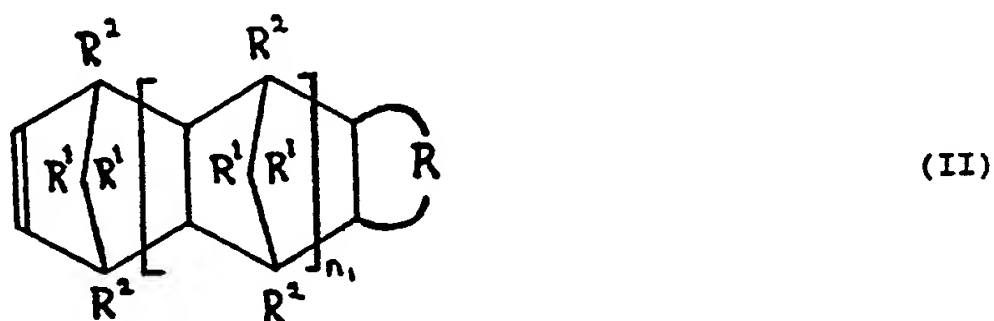
where:

R, each R¹, and each R² and n₁ are each independently as defined above

for formula (I).

The group R may be unsubstituted or substituted by one or more halogen, especially chlorine, atoms alkyl, particularly C_1 to C_4 alkyl, groups or aryl, particularly phenyl, groups. The groups R^1, and R^2 are particularly hydrogen atoms although one or more, but preferably not more than 3, of them may be halogen, especially chlorine, atoms, alkyl, particularly C_1 to C_4 alkyl, groups or aryl, particularly phenyl, groups. The index n_1 is most desirably 0 or 1, but, as is described below, the synthesis of the corresponding monomers (II) can conveniently be carried out by a Diels-Alder reaction that can lead to a mixture of monomeric species of the formula (II) thus giving an average value of n_1 which is non-integral.

We have identified various sub-classes of repeating units of the formula (I) of particular interest, notably the following repeat units of the formulae (I)a to c and the corresponding monomers (II)a to c:

(I)a

(II)a

(I)b

(II)b
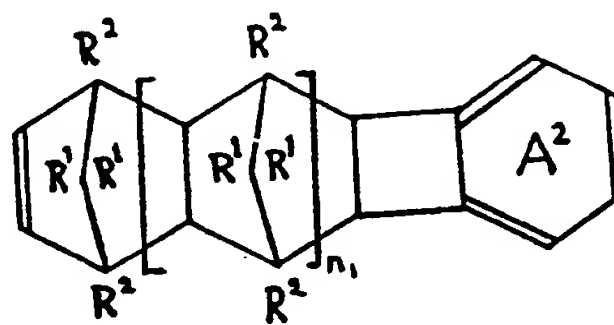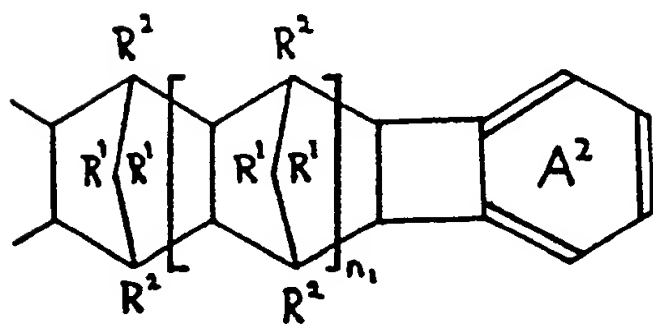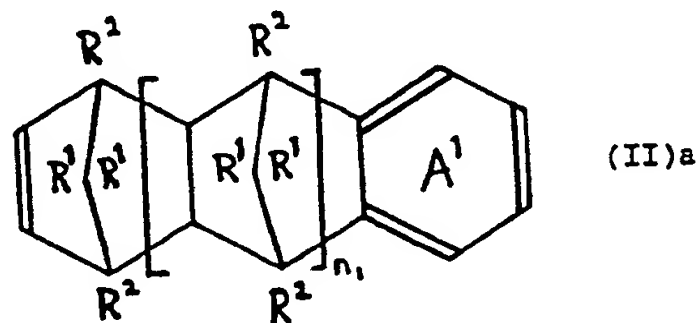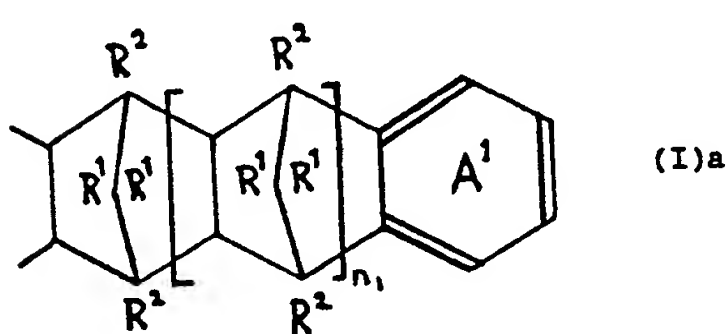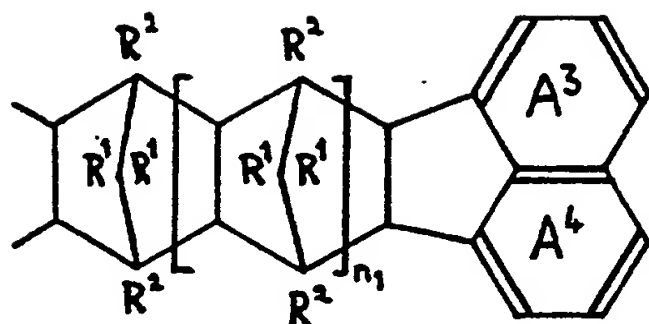
(I)c
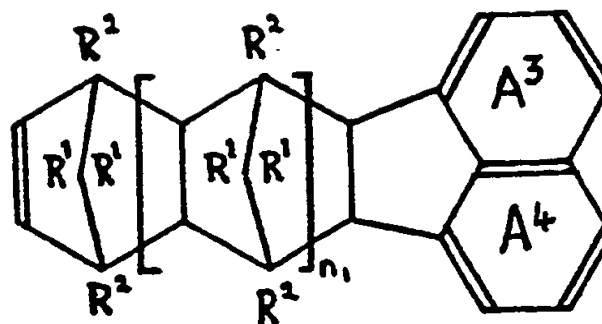
(II)c

where, for each of formulae (I)a to c and (II)a to c independently:

each R^1, each R^2 and n_1 are independently as defined above for formula (I); and the rings A^1, A^2, A^3, and A^4 independently may be substituted with one or more halogen, particularly chlorine, atoms, or C_1 to C_4 alkyl groups, or aryl, particularly phenyl, groups (as described above for the group R) and may include a further fused aromatic ring, particularly to give a corresponding benzo-ring system.

The amorphous copolymer of the invention includes units derived from at least one acyclic mono-olefin especially ethylene, propylene or a mixture of the two. Units derived from other mono-olefins, particularly alpha-olefins, e.g. C_4 to C_6 alpha-olefins, or vinyl aromatic monomers e.g. styrene or vinyl toluene, can be used although these will not normally be used to the exclusion of ethylene or propylene. Mixtures of acyclic mono-olefins, particularly alpha-olefins, and combinations of mono-acyclic olefins with relatively small proportions of other olefinic monomers can be used. In such mixtures it is desirable that the main part of units derived from the olefin [other than units of norbornene type monomers, including units of the formula (I)] are derived from ethylene and/or propylene. The other olefinic monomers are desirably at least substantially mono-olefins as the presence of di- or higher olefins will give rise to ethylenically unsaturated polymers. The presence of significant unsaturation in the polymer tends to promote undesirable propensities to cross-linking during forming processes leading to the formation of gels.

The amorphous copolymer includes units of the formula (I) above and can include units derived from other norbornene type monomers such as norbornene

itself, alkyl substituted norbornenes, such as methyl norbornene
(5-methylnorbornene) and MDMON. Unsubstituted monomers such as
dicyclopentadiene and ethylidene norbornene can be included, but the polymers
will need to be reduced to remove the ethylenic double bonds incorporated by
use of such diene monomers to avoid the moulding problems outlined above or
oxidation of the polymers after moulding.

The proportions of the norbornene type olefin and the acyclic
mono-olefin in the amorphous copolymer have a strong influence on the
properties of the polymer. If the units derived from the norbornene type
olefin represent less than about 10 mole %, the polymer product is likely to
be crystalline to a significant extent and, in practice, products containing
fractions greater than 60% of units derived from the norbornene type olefin
are difficult to prepare. The copolymers of this invention will more usually
contain from 15 to 40 mole % of units derived from the norbornene type
olefin(s). Among the units derived from the norbornene type olefin, the
proportion of units of the formula (I) will usually be at least 25% and more
usually at least 50%. Generally, within these limits, a higher proportion of
units derived from the norbornene type olefin will give a copolymer having a
higher T_g and higher rigidity.

The proportion of units derived from acyclic mono-olefin monomer(s) in
the copolymer will, correspondingly, generally be from 90 to 40 particularly
from 85 to 60 mole %. The bulk of this will typically be units derived from
ethylene. Thus, a typical copolymer will contain from 90 to 40 particularly
from 85 to 60 mole % of units derived from ethylene, although up to about
50 mole % of these units can be replaced by units derived from propylene.
The proportion of units derived from olefinic monomers, other than ethylene
and propylene, will be less than the combined proportion of ethylene and
propylene and will usually not be greater about than 10 mole % of the total
monomer content of the copolymer.

The monomers of the formula (II) above can be made by a Diels-Alder type
reaction between a suitable diene such as a cyclopentadiene and a
corresponding dienophile precursor (both substituted as appropriate for the
monomer desired). Thus, to make the monomers of the formulae (II)a to c the
dienophile precursors will be (the appropriately substituted) benzyne
(usually prepared _in situ_), benzocyclobutadiene (usually prepared _in situ_),
and acenaphthylene respectively.

The synthetic reaction is carried out under typical Diels-Alder conditions. A 1:1 molar ratio of the cyclopentadiene to dienophile precursor will give monomers having an approximate value of the index n_1 of 1. Higher values of this index can be obtained by increasing the molar proportion of the cyclopentadiene. The monomers obtained by the reaction, particularly at such higher proportions of the cyclopentadiene, will typically be a mixture of compounds of differing values of n_1 and the average value of n_1 will thus usually be non-integral.

The copolymers of the invention can be synthesised by polymerisation reactions which are generally known. Typically, the polymerisation will be carried out in the presence of a Ziegler-Natta type catalyst system. One restriction on the polymerisation is that it should avoid formation of polymer by the so-called ring opening metathesis polymerisation (ROMP) mechanism, as this makes (co-)polymers having a different structure. We have successfully used a catalyst system based on a vanadium organic ester, particularly vanadium(III)acetylacetonate [V(acac)$_3$], and an aluminium haloalkyl, particularly diethyl aluminium chloride (DEAC) in a molar ratio in the range 1:4 to 1:20, usually about 1:10. The amount of catalyst used will be chosen for best results, but will typically be from 1/200 to 1/1000 mole of the vanadium catalyst per mole of the total monomer polymerised. Typical concentrations in the polymerisation reaction mixture are about 0.1 to 5, particularly about 0.5, mmol.l^{-1} for vanadium and 1 to 50, particularly about 5, mmol.l^{-1} for aluminium.

The polymerisation reaction is typically carried out with the monomers in solution e.g. in a hydrocarbon solvent such as toluene. Conveniently, the acyclic olefin monomer(s) are introduced into the reaction mix by bubbling the gaseous acyclic olefin monomer into the solution. To reduce the chance of forming a homopolymer of the acyclic olefin monomer, which would interfere with the desired reaction e.g. by precipitating out of solution and blocking the gas inlet pipe, it is convenient to dilute the monomer with an inert carrier gas such as dry nitrogen. The reaction will typically be carried out at near or somewhat sub-ambient temperature e.g. about -30 to 30°C, especially from 0 to 10°C, although higher temperatures can be used to effect faster reaction, and in a water and oxygen free atmosphere. The reaction proceeds suitably fast, for laboratory synthesis, under atmospheric pressure although higher pressures can be used to increase the effective concentration of the

gaseous monomer(s), particularly ethylene and/or propylene.

In the polymerisation and for given reaction conditions, including the concentration of the norbornene type monomer(s), the rate of adding the acyclic olefin monomer(s) will determine the relative proportions of the norbornene type monomer(s) to the acyclic olefin monomer(s). The desired proportion will, thus, be used to decide the rate of addition of the acyclic olefin monomer(s) and the proportion of diluent gas used. As is common in this type of polymerisation reaction, gaseous hydrogen can be added as a chain transfer agent to control the molecular weight of the polymer produced. The polymerisation reaction can be carried out as a batch or as a continuous reaction.

The copolymers of the invention are amorphous polymers in which we believe the respective units derived from different monomers are distributed randomly, both in terms of the chain sequence and the stereochemistry of the side chains. They typically have T_g values in the range 50 to 200°C, especially 100 to 185°C, good stiffness properties and are substantially unaffected by water or atmospheric moisture. They can be fabricated into optical components such as optical discs, especially CD-ROM, WORM and erasable or re-writable optical discs, optical fibres and related devices and components. Accordingly the invention includes an optical component including an amorphous copolymer of or made by the method of the invention.

The following Examples illustrate the invention. All parts and percentages are by weight unless otherwise stated.

Abbreviations

Monomers:
(capital letters are solely to indicate the origin of the abbreviation)

BNBD - BenzoNorBornaDiene (systematic name: 1,4-dihydro-1,4-methano-
            naphthalene)

TMFA - 1,4,4a,10b-Tetrahydro-1,4-MethanoFluorAnthene

MDMON - 6-Methyl-1,4,5,8-DiMethano-1,4,4a,5,6,7,8,8a-OctahydroNaphthalene

Other materials:

acac - acetylacetonate e.g. vanadium(III)acetylacetonate is abbreviated
            as V(acac)$_3$

DEAC - diethylaluminium chloride

Test Methods

Proportions of respective monomers incorporated into polymers - these were derived from the ratio of aromatic to aliphatic protons measured by integration of ^{1}H nmr analysis of the copolymer. From knowledge of the structure of the monomers, the molar proportion of the residues derived from the respective monomers was calculated. The results are given as mole %, usually by quoting the ethylene content (EC).

Glass Transition temperature (T_g) - was measured by Dynamic Mechanical Analysis (DMA) (on the principles described in the Encyclopedia of Polymer Science and Engineering 2nd Edition Volume 5 at pages 299 to 329). The result quoted is the peak temperature of the loss modulus E" in °C.

Intrinsic Viscosity (IV) - was measured in decalin at 135°C and the result is quoted in dl.g^{-1}.

Synthesis Examples SE1 and SE2
Preparation of monomers

Example SE1

Synthesis of 1,4,4a,10b-tetrahydro-1,4-methanofluoranthene (TMFA)

Acenaphthylene (91.2 g; 0.6 mol), hydroquinone (0.5 g - free radical inhibitor) and trichlorobenzene (200 ml) were heated to 180°C with stirring under an atmosphere of nitrogen in a 500 ml 3-necked round bottomed flask fitted with a mechanical stirrer, thermometer, reflux condenser and pressure equalised dropping funnel containing dicyclopentadiene (39.6 g, 0.3 mol equivalent to 0.6 mol of cyclopentadiene). The dicyclopentadiene was added over a period of 30 minutes, the temperature being maintained at 175 to 180°C. The reaction mixture was held at about 180°C for a further 2 hours and then allowed to cool to ambient temperature. The product was recovered by fractional distillation under reduced pressure (1.5 mm Hg, ca. 200 Pa) to give 43 g (33% of theory) of TMFA. The structure of the product was confirmed by ^{1}H nmr and IR analysis.

Example SE2

Synthesis of 1,4-dihydro-1,4-methano-naphthalene (BNBD)

A 2 litre 3-necked round bottomed flask fitted with a mechanical stirrer, reflux condenser and two pressure equalising dropping funnels was thoroughly purged with dry nitrogen and then charged with monoglyme in a dry nitrogen atmosphere. One of the dropping funnels contained a solution of 2-aminobenzoic acid (137 g, 1.0 mol), freshly distilled cyclopentadiene (165 g, 2.5 mol) and monoglyme (300 ml) and the other contained a solution of amyl nitrite (133.3 g, 1.14 mol) and monoglyme (200 ml). The monoglyme in the flask was heated with stirring to reflux and the contents of the two dropping funnels were added dropwise at a rate to maintain gentle reflux over a period of about 3 hours. After completion of the addition, the mixture was heated under reflux for a further 3 hours and the resultant dark red solution was allowed to cool to ambient temperature. The product was recovered by

fractional distillation under reduced pressure (15 mm Hg, ca. 2 kPa) to give 70 g (50% of theory) of BNBD. The structure of the product was confirmed by ^1H nmr and IR analysis.

Examples 1 to 3
Preparation of copolymers with ethylene

In these Examples a standardised procedure for copolymerisation of norbornene type monomers with ethylene was adopted as follows:

A 1 litre flanged glass reactor fitted with a mechanical stirrer, a gas dispersion tube, a thermometer and a dropping funnel was used as the polymerisation vessel. The vessel was thoroughly purged and provided with an atmosphere of dry nitrogen, charged with dry toluene (250 ml), the norbornene type monomer(s), as set out in Table 1 below, and DEAC (2.5 mmol) and the dropping funnel was charged with V(acac)$_3$ (0.25 mmol) in dry toluene (25 ml). The vessel was cooled to 0°C and a mixture of nitrogen, at a flow rate of 36 l.h^{-1}, and ethylene, at a flow rate as set out in Table 1 below, was passed through the solution in the vessel for 10 min. The polymerisation reaction was then initiated by adding the V(acac)$_3$ solution from the dropping funnel. The nitrogen/ethylene gas flow rate was maintained for the reaction times set out in Table 1 below, with the temperature being maintained at 0°C. The reaction was then terminated by adding methanol (5 ml). The copolymer was recovered by quenching the reaction mix into a large excess of methanol (containing 0.5% by volume of 1 molar HCl and a small quantity of 2-t-butyl-4-methylphenol as antioxidant) and separating the precipitated copolymer, which was washed sequentially with methanol then with acetone and then dried under vacuum (overnight). The intrinsic viscosity, ethylene content and T_g were determined as described above and the results are included in Table 1 below.

TABLE 1

Ex No	Norbornene type monomer		Ethylene flow rate $(l.h^{-1})$	Reaction time (min)	Yield (g)	EC (mol%)	T_g (°C)	IV (dl. g^{-1})
	name	amount (mmol)						
1	TMFA	70.0	7.5	30	14.7	70	140	
2	TMFA	50.0	6.0	30	13.2	67	161	
3	TMFA MDMON	7.0 47.0	7.5	30	9.5	80	116	0.55

Claims:

1   An amorphous polymer containing units derived from an acyclic
    mono-olefin and units derived from a norbornene type olefin including
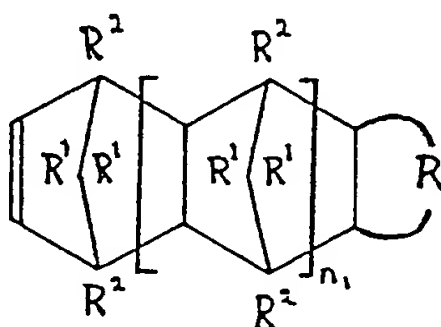   units of the formula (I):

(I)
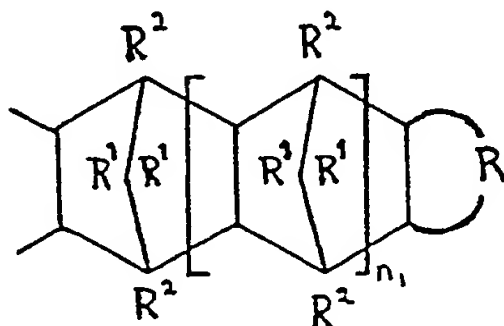
where:
    n_1 is 0,1 or 2;

    R is a divalent aromatic group; or together with the carbon atoms (of t
    bornene ring) to which it is attached forms an aromatic group ; and

    each R^1, and each R^2 is independently a hydrogen or halogen atom or
    an alkyl or aryl group.

2   An amorphous polymer as claimed in claim 1 wherein when R is a divalent
    aromatic group it is a 1,2-phenyl or a 1,8-naphthyl group; when R
    together with the carbon atoms (of the norbornene ring) to which it is
    attached forms an aromatic group it forms a 1,2-phenyl group; when R^1
    and/or R^2 are alkyl they are independently C_1 to C_4 alkyl group(s); and
    when R^1 and/or R^2 are aryl they are independently phenyl group(s).

3   An amorphous polymer as claimed in either claim 1 or claim 2 wherein R
    is substituted by one or more halogen, especially chlorine, atoms alkyl,
    particularly C_1 to C_4 alkyl, groups or aryl, particularly phenyl,
    groups.

4   An amorphous copolymer as claimed in any one of claims 1 to 3 which
     includes units derived from ethylene and/or propylene.

5   An amorphous copolymer as claimed in any one of claims 1 to 4 which
     includes units derived from at least on other norbornene type monomers,
     in particular 5-methylnorbornene and/or MDMON.

6   An amorphous copolymer as claimed in any one of claims 1 to 4 comprising
     from about 10 to about 60, particularly from about 15 to 40, mole % of
     units derived from norbornene type olefin(s) and from about 90 to about
     40, particularly from 85 to 60, mole % of units derived from acyclic
     mono-olefin monomer(s).

7   An amorphous copolymer as claimed in claim 6 wherein units of the
     formula (I) as defined in any one of claims 1 to 3 comprise at least 25,
     particularly at least 50, mole % of the norbornene type units in the
     copolymer.

8   A method of making an amorphous copolymer as claimed in any one of
     claims 1 to 7 which comprises, polymerising a mixture of at least one
     acyclic mono-olefin and at least one monomer of the formula (II):

(II)

where:
     R, each R^1, and each R^2 and n_1 are each independently as defined above
     for formula (I).